THE STRUCTURES OF THE METHYL ETHERS OF SPHINGOSINE

BY

PETER ALBERT TAVORMINA

B.S., Polytechnic Institute of Brooklyn, 1943
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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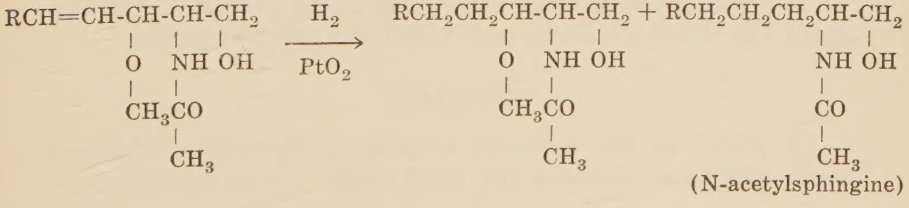
Introduction

The methanolic sulfuric acid hydrolysis of cerebrosides produces two isomeric O-methyl ethers of sphingosine. A study of the structure of these compounds was undertaken with the hope that some information might be obtained regarding the point of attachment of galactose to sphingosine in cerebrosides.

Discussion Of Results

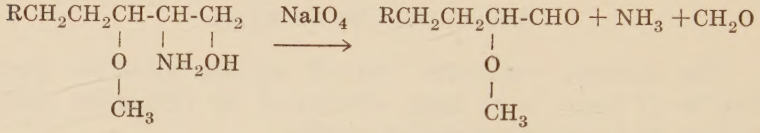
The isomers represent two of sixteen possible forms. Twelve of these have been eliminated by reduction studies and by periodate degradation studies.

Hydrogenation of either of the isomers with noble metal catalysts resulted in a mixture of reduction and hydrogenolysis products (1,2) which were difficult to separate. Reduction of the corresponding N-acetyl derivatives, however, produced similar mixtures which could be fractionated. In the case of N-acetyl-O-methylsphingosine I, the mixture was acetylated in pyridine and separated *via* fractional crystalization from hexane. The mixture resulting from the reduction of N-acetyl-O-methylsphingosine II was separated directly by fractional precipitation from acetonitrile. The hydrogenolysis product resulting from the hydrogenation of either of the isomers was D-sphingine.



Reduction of Isomer I and Isomer II (as the free bases) with Raney's nickel catalyst gave two reduced products which had the same melting point. The different rotations in chloroform of the dihydro bases, as well as the large depression in melting point exhibited by mixtures of the two reduced bases, indicated that they are different compounds despite the coincidence in their melting point. This eliminated the possibility that the two O-methyl ethers were simple *cis-trans* isomers.

Periodate oxidation of the reduced free bases yielded formaldehyde and α-methoxyheptadecanal in both cases. The possibility that the ethers were position isomers was also excluded.



The two α-methoxyheptadecanals exhibited optical activity. The one arising from reduced Isomer I had a specific rotation in hexane of $-7.7°$. The aldehyde derived from Isomer II had a specific rotation in the same solvent of $+8.6°$. These facts led to the conclusion that the isomeric O-methylsphingosines are diastereoisomers, which are epimeric at the C_3 atom.

The occurrence of geometric isomerism in addition to the optical isomerism is not excluded. On the basis of infra-red spectroscopy, it appears that the isomers are either both *cis* or both *trans*; no chemical evidence is available for or against this belief.

No studies have been made concerning which of the isomers has the threo form, and which the erythro form.

Summary

A study of the isomeric O-methylsphingosines obtained from brain cerebrosides has been made. Both isomers have

been shown to be 3-(O-methyl)-sphingosines which are epimeric at the C_3 position.

The configuration of the C_2 atom of both isomers has been shown to be the same as in D-sphingine.

The difference in configuration of the C_3 atom may be complicated by *cis-trans* isomerism, but simple *cis-trans* isomerism has been eliminated.

The occurrence of epimerism is believed due to intermediate carbonium ion formation during the replacement of the 3-hydroxyl group of sphingosine by the methoxyl group (3).

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VITA

The author was born on March 10, 1918, in Queens, New York. After graduating from Regis High School, he was employed for seven years in the Department of Purchase, City of New York. During this period he attended the Evening Session of the Polytechnic Institute of Brooklyn, receiving the Degree of Bachelor of Science in Chemistry in 1943. In 1942 he entered the armed forces, serving as meteorologist in the Army Air Forces. Upon discharge from the army in 1946, he entered the graduate school of the University of Illinois, where he held a teaching assistantship from June, 1946, until June, 1947, and a research assistantship from October, 1948, to June, 1949.

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